NASA Technical Memorandum 104099

LaRC-ITPI/Arylene Ether Copolymers

Brian J. Jensen
Dennis C. Working

May 1991

National Aeronautics and
Space Administration

Langley Research Center
Hampton, Virginia 23665-5225

LaRC-ITPI/Arylene Ether Copolymers

by

B. J. Jensen

NASA Langley Research Center

Hampton, VA 23665-5225

and

D. C. Working

Analytical Services and Materials, Inc.

Hampton, VA 23666

Introduction

As part of an effort to develop high performance structural resins for aerospace applications, work has continued on block copolymers containing imide and arylene ether segments. The copolymers reported herein represent an extension of previous work[1-3] on imide/arylene ether copolymers. The arylene ether block used in this study contains a bulky fluorene group in the polymer backbone while the imide block contains an arylene ketone segment similar to that in the arylene ether block and has been named LaRC-ITPI[4]. A few copolymers containing an imide block and some other block have been reported. Most notably, the copolymers containing imide and siloxane blocks have received considerable attention[5-8] and more recently, polyimide-polyformal block copolymers[9] and triblock copolymers containing imide-aryl ether phenylquinoxaline blocks[10] have been

reported. The preparation of amine-terminated sulfones by a method similiar to that used herein has been reported.[11]

Experimental

Monomers - 9,9-Bis(4-hydroxyphenyl)fluorene (BPF) was synthesized as previously reported[12] and recrystallized from toluene to yield an off-white solid (m.p. 222-223.5°C). 1,3-Bis(4-fluorobenzoyl)benzene (FBB) was synthesized as previously reported[12] and recrystallized from toluene to yield a white crystalline solid (m.p. 178-179°C). 4-Aminophenol was obtained commercially and vacuum sublimed to yield an off-white solid (m.p. 188-190°C). 4,4'-Isophthaloyldiphthalic anhydride (IDPA) (m.p. 215-217°C) was obtained from Allco Chemical and used as received. m-Phenylenediamine (m-PDA) was obtained commercially and vacuum sublimed to yield a white crystalline solid (m.p. 64-66°C). 3,3',4,4'-Benzophenonetetracarboxylic dianhydride (BTDA) was obtained commercially and vacuum sublimed to yield a white crystalline solid (m.p. 224-226°C).

Oligomers - The amine-terminated poly(arylene ethers) (ATPAE) were synthesized as shown in Eq. 1 by aromatic nucleophilic substitution of FBB with BPF and 4-aminophenol in N,N-dimethylacetamide (DMAc) using potassium carbonate. The oligomers were prepared at two different calculated molecular weights ($\bar{M}n$) by adjusting the monomer ratio (BPF/FBB) to 0.816 and 0.908 to provide $\bar{M}n$ of 3110 and 6545 g/mole, respectively. The anhydride-terminated poly(amic acids) were prepared in DMAc at two $\bar{M}ns$ as shown in Eq. 2 by adjusting the monomer ratio (m-PDA/IDPA) to 0.842 and 0.923 to provide $\bar{M}n$ of 3110 and 6545 g/mole, respectively.

Copolymers - The copolymers were prepared by adding a DMAc solution of the ATPAE to the anhydride terminated m-PDA/IDPA reaction mixture. For example, to

prepare ATPAE 3110/ITPI 3110, IDPA (2.1317 g, 5.0 mmol) was added to a solution of m-PDA (0.4552 g, 4.21 mmol) and DMAc (14.7 g). The mixture was stirred for 3 h to form a clear solution. A solution of ATPAE 3110 (2.5867 g, 0.8318 mmol) in DMAc (14.7 g) was added to the poly(amic acid) solution prepared above to form a clear, viscous solution. On occasion, some reactions became very viscous and gelled within ~10 min, but additional stirring (normally overnight but sometimes for several days) or warming to ~70°C provided a clear viscous solution. These solutions were used to cast films which were thermally imidized.

Characterization - Inherent viscosities (η_{inh}) were obtained on 0.5% solutions in $CHCl_3$ at 25°C for FBB/BPF and in DMAc at 25°C for the other polymers and copolymers. Differential scanning calorimetry (DSC) was performed at a heating rate of 20°C/min with the apparent T_g taken at the inflection point of the ΔT versus temperature curve. Torsional braid analysis (TBA) was performed at a heating rate of 3°C/min with the T_g taken at the peak of the damping curve.

Films - DMAc solutions (15% solids) of the polymers were centrifuged, the decantate doctored onto plate glass and dried at room temperature to a tack-free form in a dust proof chamber. The films on glass were dried 1 h each at 100, 200 and 300°C. Mechanical tests were performed according to ASTM D882 on at least four specimens per test condition.

Results and Discussion

ATPAEs with calculated $\overline{M}_n$s of 3110 and 6545 g/mole were prepared by offsetting monomer stoichiometry. These oligomers had η_{inh}s of 0.18 and 0.30 dL/g and T_gs of 193 and 207°C, respectively, as shown in Table I. When the oligomers were reacted with a stoichiometric amount of BTDA, the η_{inh}s and T_gs increased as

expected. The high η_{inh}s obtained indicated that the calculated $\bar{M}_n$s were essentially correct. Table I also shows data for the homopolymers and a 1:1 physical blend of the homopolymers prepared by mixing DMAc solutions of each. This blend phase separated in solution as well as in the cured film. A DSC sample containing both phases displayed the two T_gs of the homopolymers.

Four different block copolymers were prepared as shown in Table II from the ATPAE and ITPI oligomers. The copolymers were prepared by reacting a stoichiometric ratio of oligomers (using calculated $\bar{M}_n$s) producing poly(amic acids) with η_{inh}s ranging from 0.63 to 0.91 dL/g in DMAc. The cured polyimide films were characterized by DSC and results are shown in Table II. T_gs range from 224 to 257°C with the ATPAE 6545/ITPI 6545 block copolymer displaying two T_gs, slightly above and below the T_gs of the FBB/BPF and ITPI, respectively. Block copolymers with shorter imide blocks display a DSC T_g slightly above the T_g of the FBB/BPF homopolymer while the block copolymer with the shorter arylene ether block and the longer imide block displays only the T_g slightly below that of the ITPI homopolymer (253°C). Apparent T_gs by TBA are also shown in Table II and range from 246 to 254°C after curing the braids 1 h each at 100, 200 and 300°C. Copolymer with longer imide blocks display higher transition temperatures than those with shorter imide blocks as expected.

Two segmented copolymers, ATPAE 3110/ITPI 3110 (segmented) and ATPAE 6545/ITPI 6545 (segmented) were prepared by dissolving the ATPAE and m-PDA in DMAc and then adding the appropriate amount of IDPA to the solution. The m-PDA/IDPA ratios were adjusted to give a $\bar{M}n$ of either 3110 or 6545 g/mole, the same $\bar{M}n$ as the ATPAE block. As shown in Table II, very high η_{inh}s were obtained from these reactions. When characterized by DSC, cured films of the ATPAE 3110/ITPI 3110 (segmented) copolymer had a T_g = 230°C while cured films

of the ATPAE 6545/ITPI 6545 (segmented) copolymer had T_gs at both 230 and 255°C, similar to that of the ATPAE 6545/ITPI 6545 block copolymer.

Tensile properties of the clear yellow-orange films of the copolymers and homopolymers are shown in Table III. The polyimide has higher strength and modulus than the arylene ether as expected. The tensile strength and modulus of the copolymers varied widely. The ATPAE 6545/ITPI 6545 block copolymer produced a phase-separated textured film with very poor properties while the ATPAE 6545/ITPI 3110 displayed excellent retention of strength at 177°C and very high modulus at RT and 177°C. The other films displayed properties intermediate to those of FBB/BPF and ITPI homopolymers.

Conclusions

A series of imide/arylene ether block and segmented copolymers were prepared using an arylene ether block with a relatively high T_g and an imide block with high mechanical properties. A 1:1 blend of high molecular weight homopolymers was incompatible in DMAc solution and in the solid state. One block copolymer displayed higher film properties than either homopolymer while the remaining copolymers displayed properties which were intermediate to those of the homopolymer.

REFERENCES

1. B. J. Jensen, P. M. Hergenrother and R. G. Bass, Proc. Polym. Matl. Sci. and Eng., 60, 294 (1989).
2. B. J. Jensen, P. M. Hergenrother and R. G. Bass, Polym. Prepr., 30(2), 132 (1989).
3. B. J. Jensen, P. M. Hergenrother and R. G. Bass, Ibid., 31(1) 618 (1990).
4. J. R. Pratt and T. L. St. Clair, SAMPE Journal, 26(6), 29(1990).
5. F. F. Holub, U. S. Patent 3,325,450 (1967) (To General Electric).
6. W. A. Fessler, U. S. Patent 3,736,290 (1973) (To General Electric).
7. J. T. Hoback and F. F. Holub, U. S. Patent 3,740,305 (1973) (To General Electric).
8. I. Yilgor, E. Yilgor, B. C. Johnson, J. Eberle, G. L. Wilkes and J. E. McGrath, Polym. Prepr., 24(2), 78(1983).
9. M. M. Grade and J. W. Verbicky, Jr., J. Polym. Sci., Polym. Chem. Ed., 27, 1467 (1989).
10. J. L. Hedrick and J. W. Labadie, High Performance Polymers, 2(1), 3 (1990).
11. J. H. Kawakami, G. T. Kwiatkowski, G. L. Brode and A. W. Debroin, J. Polym. Sci., Polym. Chem. Ed., 12, 565 (1974).
12. P. M. Hergenrother, B. J. Jensen and S. J. Havens, Polymer, 29, 358(1988).

TABLE I. CHARACTERIZATION OF OLIGOMERS AND POLYMERS

Oligomer or Polymer	η_{inh}, dL/g	T_g, °C by DSC
ATPAE 3110	0.18	193
ATPAE 6545	0.30	207
ATPAE 3110/BTDA	1.16	226
ATPAE 6545/BTDA	1.40	227
ITPI	0.50	262
FBB/BPF	0.68 ($CHCl_3$)	223
ITPI//FBB/BPF Blend	------	223,262

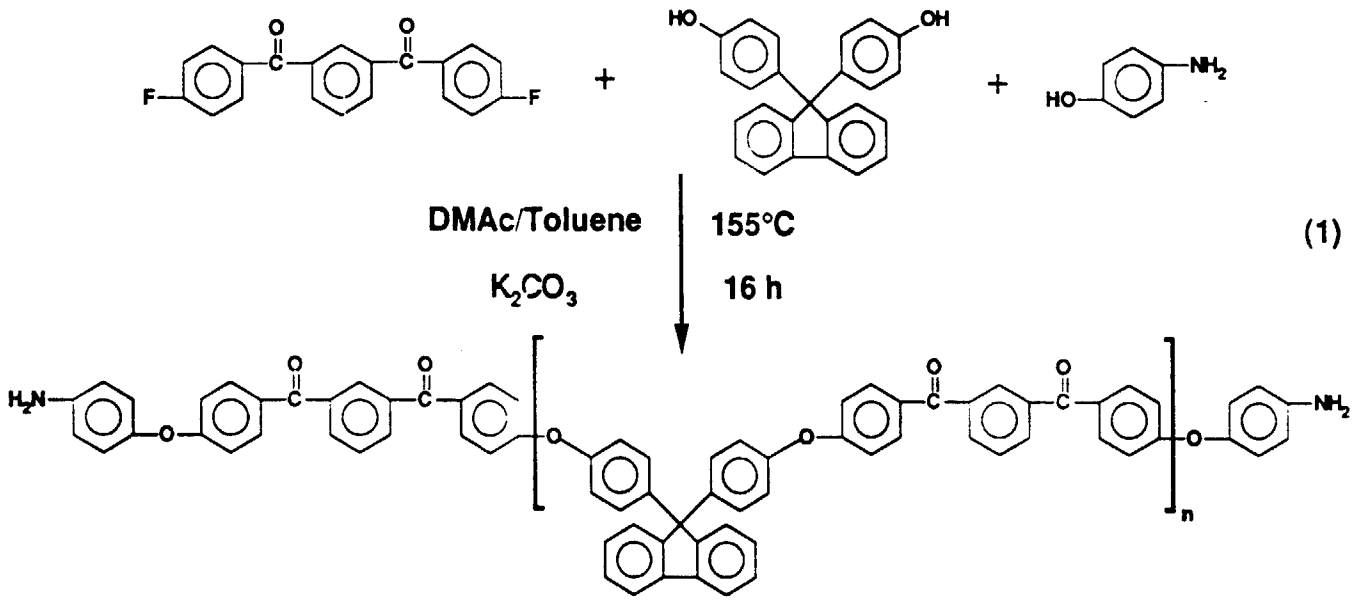
TABLE II. CHARACTERIZATION COPOLYMERS

Copolymer	η_{inh}, dL/g (Polyamic acid)	T_g, °C by DSC	T_g, °C by TBA
ATPAE 3110/ITPI 3110	0.72	224	246
ATPAE 3110/ITPI 6545	0.63	253	254
ATPAE 6545/ITPI 3110	0.91	228	248
ATPAE 6545/ITPI 6545	0.84	230,257	253
ATPAE 3110/ITPI 3110 (Segmented)	1.37	230	249
ATPAE 6545/ITPI 6545 (Segmented)	1.54	230,255	254

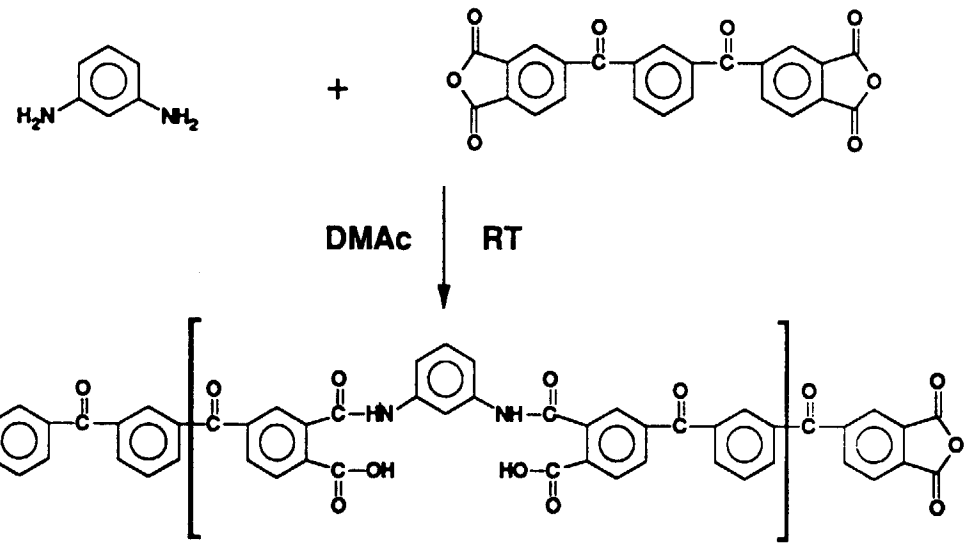
Table III. FILM PROPERTIES

Polymer	Tensile Strength, ksi		Tensile Modulus, ksi		Elongation, %	
	RT	177°C	RT	177°C	RT	177°C
ATPAE 3110/BTDA	10.3	6.8	413	374	3.3	3.0
ATPAE 6545/BTDA	11.9	6.2	400	321	3.8	3.4
ATPAE 3110/ITPI 3110	18.7	12.2	547	436	8.3	7.5
ATPAE 3110/ITPI 6545	19.0	12.1	520	443	5.6	5.7
ATPAE 6545/ITPI 3110	26.8	22.7	752	550	5.5	10.0
ATPAE 6545/ITPI 6545[1]	5.6	2.7	319	135	2.6	8.3
ATPAE 3110/ITPI 3110 (Segmented)	21.2	12.0	475	197	8.0	10.0
ATPAE 6545/ITPI 6545 (Segmented)	20.8	12.2	400	382	8.0	18.0
ITPI	31.0	17.9	640	266[2]	12.8	15.7
FBB/BPF	13.5	5.5	378	304	4.6	2.5

[1]Phase separated film.
[2]Lit[4] value of 380 ksi at 200°C.



ATPAE



m-PDA/ODPA

NASA National Aeronautics and Space Administration

Report Documentation Page

1. Report No.	2. Government Accession No.	3. Recipient's Catalog No.
NASA TM-104099		

4. Title and Subtitle	5. Report Date
LaRC-ITPI/Arylene Ether Copolymers	May 1991
	6. Performing Organization Code

7. Author(s)	8. Performing Organization Report No.
Brian J. Jensen and Dennis C. Working	
	10. Work Unit No. 505-63-50-01

9. Performing Organization Name and Address	11. Contract or Grant No.
NASA Langley Research Center Hampton, VA 23665-5225	
	13. Type of Report and Period Covered
12. Sponsoring Agency Name and Address	Technical Memorandum
National Aeronautics and Space Administration Washington, DC 20546-0001	14. Sponsoring Agency Code

15. Supplementary Notes

Use of trade names or names of manufacturers does not constitute an official endorsement of such products or manufacturers, either expressed or implied, by the National Aeronautics and Space Administration

Brian J. Jensen: NASA Langley Research Center, Hampton, Virginia
Dennis C. Working: Analytical Services and Materials, Hampton, Virginia

16. Abstract

As part of an effort to develop high performance structural resins for aerospace applications, work has continued on block copolymers containing imide and arylene ether segments. The arylene ether block used in this study contains a bulky fluorene group in the polymer backbone while the imide block contains an arylene ketone segment similar to that in the arylene ether block and has been named LaRC-ITPI. A series of imide/arylene ether block and segmented copolymers were prepared and characterized. Films were prepared from these copolymers and mechanical properties were measured.

17. Key Words (Suggested by Author(s))	18. Distribution Statement
Polyimides, Poly(arylene ethers), Copolymers, and Block Copolymers	Unclassified - Unlimited Subject Catagory - 27

19. Security Classif. (of this report)	20. Security Classif. (of this page)	21. No. of pages	22. Price
Unclassified	Unclassified	11	A03